

# COATINGS. ENAMELS

UDC 666.293

## FORMATION OF CONTACT LAYERS DURING PRE-TREATMENT OF ALUMINUM BY CHROMATING BEFORE ENAMELING

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Several methods of preparing an aluminum surface prior to single-layer enameling are examined. A method is developed for preparing an aluminum surface by alkali chromate oxidation in a solution based on  $K_2Cr_2O_4$  without annealing but with pre-degreasing with formation of complexes of the type  $[Al(OH)_4(H_2O)_2]^-$ ,  $[Al(OH)_6]^{-3}$ , and  $[Al(OH)_5(H_2O)]^{-2}$ . The effect of the preparation methods on the quality of the enamel coating is studied. The mechanism of the formation of nano-dispersed layers of solid solutions which promote stable bonding of a coating to aluminum is studied.

**Key words:** single-layer enameling, enamel coatings, bonding of enamel with metal, intermediate layer, degreasing, chromating.

The formation of high-quality enamel coatings depends on the physical-chemical processes that give, first and foremost, a strong bond with steel. A. A. Appen singles out three basic factors for enamel–steel bonding: adhesion interaction, role of the surface relief of the substrate, and the chemical nature of the transition layer formed. For this reason, to improve the bonding the metal surface is subjected to special treatment before enameling — cleaning, degreasing, imparting a special relief by etching, sand blasting, creating various films (nickel plating, borating, zinc plating, and others) [1].

However, at the present time not only is it necessary to ensure a strong bond but the enamel–steel bond must be quite flexible. For this, single-layer enameling is most promising as compared with the conventional double-layer enameling. In the case of two-layer enameling, bonding oxides, such as  $CoO$ ,  $NiO$ ,  $Cr_2O_3$ , and  $MnO_2$  — at present coloring oxides which must be excluded in single-layer white enameling, are introduced into the base layer. For this reason, the stage of preliminary treatment of the metal becomes paramount for ensuring good enamel–steel bonding, and the methods used to treat the steel before depositing the enamel which are used for two-layer enameling are inadequate for single-layer white enameling.

In connection with the growth in the construction of multifloor buildings and structures, aluminum and alumi-

num-based alloys are widely used as construction materials because of their lightness. Cookware made of stamped and cast aluminum coated on the inside with an antistick teflon coating for cooking with minimum fat and oil is now ubiquitous. These and other areas of application of aluminum and its alloys require the synthesis of heat- and chemical-resistant enamels with a wide range of colors.

Enameling of pure aluminum does not require such multistage pre-treatment of a surface as compared with enameling steel, since aluminum oxidizes less easily than iron and copper: for high-temperature gas corrosion it is coated with an  $Al_2O_3$  film, which possesses protective properties. To 400°C aluminum follows a logarithmic law of oxidation, while above 400°C it follows an inverse logarithmic law. The main condition characterizing the capability of a formed, primary, oxide film to stop further oxidation of metal is the continuity of the oxide film obtained [2]. If the volume  $V_{ox}$  of the chemical compound of the film material, for example, an oxide, is less than the volume  $V_m$  of the metal from which this film arose, then a discontinuous, porous, and therefore poorly-protecting film can be expected to form. Conversely, for film volume large compared with the metal there are reasons for expecting the formation of continuous, more protective films. For aluminum the volume ratio of the oxide formed and of the initial metal  $V_{ox}/V_m = 1.28$ . However, defects also form on the surface of enameled aluminum.

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TABLE 1. Composition of Glasses for Enameling [6]

Composition	Content, wt.%						
	Na <sub>2</sub> O	Li <sub>2</sub> O	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>
1	19.70	1.97	7.88	29.55	9.85	29.55	1.48
2	13.14	1.32	5.25	29.55	12.32	36.94	1.48
3	15.70	1.57	6.28	27.59	11.82	35.46	1.48
4	26.27	2.63	10.51	19.70	9.85	29.55	1.48
5	19.70	1.97	7.88	19.70	12.32	36.94	1.48
6	13.14	1.32	5.25	19.70	14.78	44.33	1.48
1-1	19.61	1.96	7.84	29.41	9.80	29.41	1.96
2-1	13.07	1.31	5.24	29.41	12.25	36.76	1.96
3-1	15.68	1.57	6.28	27.45	11.76	35.29	1.96
4-1	26.14	2.61	10.46	19.61	9.80	29.41	1.96
5-1	19.61	1.96	7.84	19.61	12.25	36.76	1.96
6-1	13.07	1.30	5.23	19.61	14.71	44.10	1.96
1-2	19.51	1.95	7.80	29.27	9.75	29.27	2.44
2-2	13.00	1.30	5.20	29.27	12.19	36.59	2.44
3-2	15.62	1.56	6.24	27.32	11.70	35.12	2.44
4-2	26.01	2.61	10.41	19.51	9.75	29.26	2.44
5-2	19.51	1.95	7.80	19.51	12.19	36.59	2.44
6-2	13.00	1.30	5.20	19.51	14.63	43.91	2.44

There are different variants of surface preparations of aluminum and its alloys for enameling. All methods pursue the same goal — to ensure good enamel – metal bonding. For pure aluminum, as a rule, only surface degreasing is sufficient, while enameling alloys requires additional treatment which improves the structure of the surface oxide film. The following operations are performed to prepare a metal surface to improve the bond with enamel: degreasing, laving, deposition of metal films, phosphate coating, oxidation, specifically chromate treatment, annealing, and others [3, 4]. The most widely used method for surface treatment of aluminum is chromating, which is used to create a conversion layer that improves the adhesion of metal with enamel. There are several methods of chromating with the participation hexavalent chromium ions, specifically, alkali treatment using K<sub>2</sub>CrO<sub>4</sub> and acidic treatment using CrO<sub>3</sub> or Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Chromating forms on the surface of aluminum a dense, strong, passivating oxide film, strong bonded with the metal and creating a good adhesion base for coating deposition.

According to research data, the following surface treatment is optimal for Al [5]:

1st step) degreasing in a solution with the composition (g/liter): Na<sub>3</sub>PO<sub>4</sub> — 50 and Na<sub>2</sub>CO<sub>3</sub> — 50; solution temperature 60 – 70°C; treatment time 5 min;

2nd step) laving with hot and cold water;

3rd step) oxidation, chromating in solution (g/liter): K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> — 15; NaOH — 2.5; Na<sub>2</sub>CO<sub>3</sub> — 50; solution temperature 85 – 95°C; treatment time 15 – 20 min.

Mechanical stream working with corundum is used for the inner surface of articles coated with Teflon.

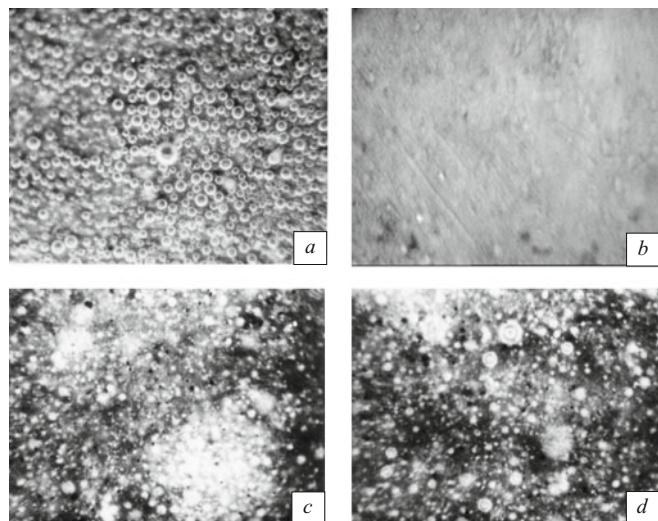


Fig. 1. Photomicrography of the surface of enameled samples (glass composition No. 3-1) after surface treatment by the method: a) I; b) II; c) IV; d) V,  $\times 500$ .

The results of studies of the effect of different methods of surface treatment of aluminum on the quality of the glass-enamel coatings based on the phosphate glass compositions Nos. 3, 3-1, and 3-2 developed (Table 1) are presented in Table 2. For this, enamel slip was deposited by immersion on prepared samples of aluminum. Next, after drying the sample were heat-treated at temperatures 450 – 550°C for 5 – 6 min depending on the composition.

Figure 1 shows photomicrographs of the surface of enameled samples (glass composition No. 3-1) after surface treatment by the methods I, II, IV, and V. Analysis of the results showed that degreasing followed by annealing without additional processing (method I) gives a strong enamel – metal bond, but strong blistering of enamel with formation of large bubbles is observed (Fig. 1a). High-quality coatings could not be obtained by processing with an acidic chromate solution; there was no bonding with the metal, wetting was incomplete, and the coatings contained many gas bubbles of different size (Fig. 1c and d). Separation and chipping of the coatings are observed when these treatments are used. At the same time, for alkaline chromate oxidation without subsequent annealing (method II) the coatings spread well over the surface of the metal, do not blister, i.e., they have no bubble inclusions and do not separate, the bonding strength is not less than 85%, and they have a good sheen (Fig. 1b). Thus the best surface-preparation method of those studied for aluminum is alkaline chromate oxidation without annealing (method II).

To study the bonding mechanism for enameling of aluminum and to develop a model for the formation of an intermediate layer and determine the possibility of formation of fractal structures for activation of bonding, the role of each step of surface treatment by alkaline chromate oxidation in the formation of a low-melting coating was determined. Fi-

TABLE 2. Effect of the Method Used to Treat Metal Surfaces on Coating Formation

Treatment method	Solution	Treatment stages, composition, g/liter	Temperature, °C	Duration, min	Coating characteristics
Degreeing					
I	Alkaline soda	1. $\text{Na}_2\text{CO}_3$ — 52.7	90	10	Strong blistering, large bubbles, strong bond
		2. Annealing	500	5	
Chromate oxidation					
II	Alkaline chromate	1. $\text{Na}_2\text{CO}_3$ — 50; $\text{Na}_3\text{PO}_4$ — 50.	85 — 90	5	No blistering, good sheen, strong bond
		2. Washing with hot water.			
		3. $\text{Na}_2\text{CO}_3$ — 50; $\text{K}_2\text{CrO}_4$ — 25; $\text{NaOH}$ — 20	60 — 70	15 — 20	
III	Acidic chromate	1. $\text{Na}_2\text{CO}_3$ — 50; $\text{Na}_3\text{PO}_4$ — 50.			Coating separates, many gas inclusions
		2. Washing with hot water.			
		3. $\text{H}_3\text{PO}_4$ — 12; $\text{NaF}$ — 3.1. Chromium anhydride — 3.6.	50	15	
		4. Annealing	500	5	
IV		1. $\text{Na}_2\text{CO}_3$ — 50; $\text{Na}_3\text{PO}_4$ — 50.			Strong blistering, no bond
		2. Washing with hot water.			
		3. $\text{H}_3\text{PO}_4$ — 12; $\text{NaF}$ — 3.1. Chromium anhydride — 3.6	50	15	
		1. $\text{Na}_2\text{CO}_3$ — 50; $\text{Na}_3\text{PO}_4$ — 50.			
V		2. Washing with hot water.			Individual gas inclusions, no bond
		3. $\text{Na}_2\text{CO}_3$ — 60.0; $\text{Na}_2\text{Cr}_2\text{O}_7$ — 20.0; $\text{Na}_2\text{HPO}_4$ — 2.0.	90	15	
		4. Washing with hot water.			
		5. Annealing	500	5	

Figure 2 shows photomicrographs of the surface of an enamel coating after each treatment step.

The quality of the surface of the enamel coating after the first treatment step using a phosphate-soda solution without washes (Fig. 2c) and followed by washing (Fig. 2b) is unsatisfactory because of the formation of a large quantity of gas inclusions. Only subsequent surface treatment of the metal in an alkaline chromate solution made it possible to obtain an enamel coating of good quality (Fig. 2c).

Such a difference in coating quality at different stages of treatment of the metal can be explained by the difference between the mechanism of the reactions occurring on an aluminum surface undergoing enameling. Probably, at the degreasing stage the oxide film of the aluminum interacts with the alkali, forming hydroxy-complexes via the reaction  $\text{Al}_2\text{O}_3 + 2\text{OH}^- + 7\text{H}_2\text{O} \leftrightarrow 2[\text{Al}(\text{OH})_4(\text{H}_2\text{O})]^-$ , and less stable complexes  $[\text{Al}(\text{OH})_6]^{-3}$  and  $[\text{Al}(\text{OH})_5(\text{H}_2\text{O})]^{-2}$  can likewise form. These reactions partially destroy the surface oxide layer, denuding the surface of the metallic aluminum,

which, in turn, actively interacts with water with hydrogen gas being formed, which is the reason why bubbles appear in the enamel (Fig. 2a). After the surface of the sample is laved in hot water these products are removed from the aluminum surface, since they are not strongly bound with the substrate, denuding the aluminum surface even more. Even though an oxide film forms rapidly on these sections of the aluminum surface, under the conditions of the present experiment the required film thickness is not reached, and on some sections the aluminum can remain unprotected and can actively interact with the components of the enamel and with moisture with gases being released. In the process, the enamel melt wets the aluminum surface nonuniformly, and the enamel can have numerous defects in the form of a large number of bubbles (Fig. 2b).

When chromating is performed with the solution (g/liter)  $\text{Na}_2\text{CO}_3$  — 50,  $\text{K}_2\text{CrO}_4$  — 25, and  $\text{NaOH}$  — 20 a number reactions occur that change the chemical composition of the surface layer of the metal and improve the spreading of

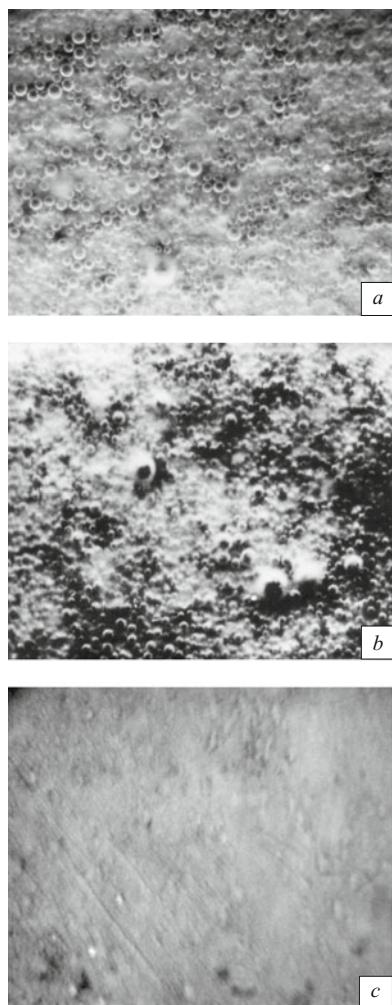
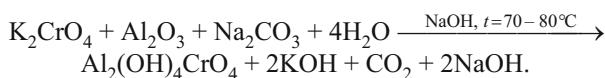


Fig. 2. Photomicrographs of the surface of an enamel coating on aluminum after different treatment stages of the method II: a) degreasing; b) degreasing, washing; c) degreasing, washing chromate treatment,  $\times 500$ .

the enamel melt over the surface of the aluminum. Very likely, on heating to  $70 - 80^\circ\text{C}$  the composition used for treating the metal at step 3 reacts with the aluminum oxide in the main medium of sodium hydroxide and forms complex compounds of chromium (VI) oxide and aluminum, destroying the oxide film via the reaction



Calculations show that the Gibbs energy for this reaction is  $-300.56 \text{ kJ/mole}$  at  $80^\circ\text{C}$ .

Thus a layer of the complex compound  $\text{Al}_2(\text{OH})_4\text{CrO}_4$  very likely forms on the surface of the metal. This compound interacts with the surface aluminum via the oxidation-reduction reaction

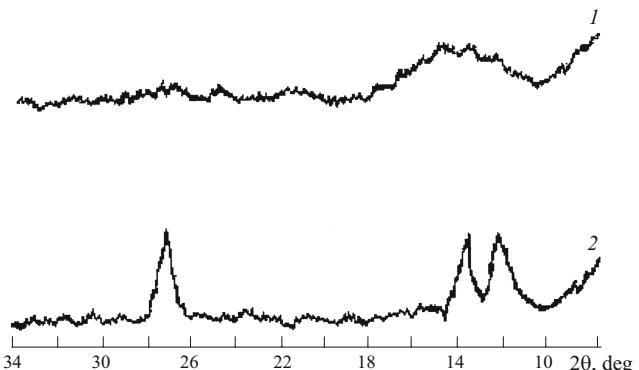


Fig. 3. Diffraction pattern of a chromate aluminum sample before (1) and after (2) heat-treatment at  $500^\circ\text{C}$  for 30 min.

and then during heat-treatment it decomposes via the dehydration reaction

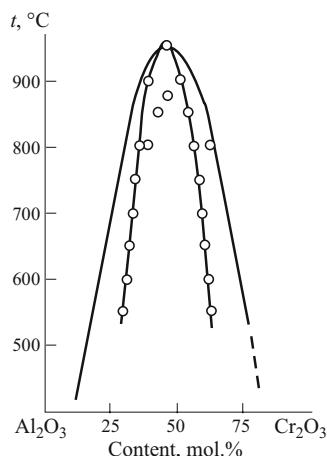


The product of this reaction  $\text{Al}_2(\text{CrO}_4)_3$  also interacts with aluminum via an oxidation-reduction reaction



Only an amorphous halo (Fig. 3, curve 1) is observed in the diffraction patterns of the reaction products without heat-treatment. This indicates ultradispersity of the chromium and aluminum oxides formed via the reaction (1), i.e., the oxides formed have an elevated reactivity. After heat-treatment at  $500^\circ\text{C}$  for 30 min the XPA (Fig. 3, curve 2) showed the presence of reflection of quite well formed crystalline phase in the cubic system with lattice parameter  $a = 4.00 \pm 0.02 \text{ \AA}$ . The character of the diffraction pattern corresponds to that of  $\gamma\text{-Al}_2\text{O}_3$ . It is known that the structure of  $\gamma\text{-Al}_2\text{O}_3$  is that of defective spinel with cubic cell parameters  $a = 3.95 \text{ \AA}$  [5]. Thus the phase discovered is a solid solution based on  $\gamma\text{-Al}_2\text{O}_3$  formed via the reaction  $(1-x)\text{Al}_2\text{O}_3 + x\text{Cr}_2\text{O}_3 \rightarrow \text{Al}_{2(1-x)}\text{Cr}_{2x}\text{O}_3$ . The formation of such solid solutions corresponds to the phase diagram of equilibria in the system  $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$  (Fig. 4), according to which at temperatures above about  $950^\circ\text{C}$  there exists a continuous series of solid solutions, while below this temperature there is a region of immiscibility of solid solutions based on the phase  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . The extent of the solid solutions at  $500^\circ\text{C}$  is (molar content, %) about 25  $\text{Cr}_2\text{O}_3$  (based on  $\gamma\text{-Al}_2\text{O}_3$ ) and about 35  $\text{Al}_2\text{O}_3$  (based on  $\text{Cr}_2\text{O}_3$ ).

According to the reactions (1) and (3) the amount of the active  $\text{Al}_2\text{O}_3$  formed is several-fold (about 5-fold) greater than the content of  $\text{Cr}_2\text{O}_3$  and therefore the composition of the phases formed during calcination falls into the region of existence of the solid solutions with concentration above 75% (molar content)  $\text{Al}_2\text{O}_3$  at temperature  $500^\circ\text{C}$ , which confirms the character of the phase formation during heat



**Fig. 4.** Subsolidus phase diagram of the system  $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ : ○ region of immiscibility of solid solutions according to the experimental data; — computation method of [7].

treatment of the chromated surface. This mechanism very likely remains during enameling.

An estimate of the average grain size according to the integral width of the main reflection, as calculated by Scherrer's method, gives 20 – 25 nm.

Thus the solid-solution layer formed is nano-disperse, which should promote a strong metal – layer bond on the one hand and an enamel – layer bond, as a result of active interaction with the components of the enamel, on the other.

The investigations show that the optimal method is to prepare the surface of aluminum by means of alkali chromate oxidation in a  $\text{K}_2\text{Cr}_2\text{O}_4$  based solution without annealing

but with preliminary degreasing with formation of complexes of the type  $[\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2]^-$ ,  $[\text{Al}(\text{OH})_6]^{-3}$ , and  $[\text{Al}(\text{OH})_5(\text{H}_2\text{O})]^{-2}$ . It was found that during the subsequent chromating nanodisperse solid solutions of the type  $\text{Al}_{2(1-x)}\text{Cr}_{2x}\text{O}_3$  are formed via a series of reactions. These solutions promote strong bonding of aluminum with the coating and, in consequence, they also promote the formation of a high-quality enamel coating.

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